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## **ABSTRACT**

Contaminated groundwater resulting from pyrite oxidation of acid sulphate soils (ASS) is a major environmental problem in coastal Australia. A column test was carried out for an extended period with recycled concrete to study the efficiency of the reactive materials for neutralising acidic groundwater. Results show that the actual acid neutralisation capacity of the recycled concrete could decrease to less than 50% of the theoretical value due to armouring effects. Nevertheless, the performance is good as a spot treatment in Acid Sulphate Soil Terrain utilising a near-zero cost waste product. Based on the test results and site characterisation, a PRB with recycled concrete was designed and installed in ASS terrain on the Shoalhaven River floodplain, southeastern, Australia in October 2006. The performance of the PRB was studied over two and half years to assess the potential of recycled concrete (i) to neutralise the groundwater acidity and (ii) to remove the dissolved heavy metals such as iron and aluminium from *in situ* acidic groundwater. To date, performance monitoring of the PRB shows that recycled concrete can successfully improve the pH of groundwater from acidic to mildly alkaline. In addition, it successfully removes groundwater iron and aluminium. Results reported here also reveal a slow decrease in the performance of the PRB due to armouring effects probably caused by precipitation of iron and aluminium on the surface of the reactive recycled concrete materials.

Key words: acid sulphate soils, armouring effects, contaminated groundwater, permeable reactive barrier.

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## INTRODUCTION

Acidic groundwater, generated from acid sulphate soil (ASS) is a major environmental problem in Australia. ASS occupies over 200,000 km<sup>2</sup> of the Australian landscape, of which approximately 30% is coastal (White et al. 1997). The total area of ASS in Australia is estimated to contain 700 million tonnes of potentially environmental hazardous sulphidic material (commonly pyrite). If left undisturbed and submerged under the watertable, this pyritic material is relatively chemically inert. However, disturbance and drainage of sulphidic soils can cause oxidation of pyrite and generation of sulphuric acid in the soil (Lin et al. 1995). In fact, the total amount of pyritic material in the Australian landscape is equivalent to about 2.2 billion tonnes of sulphuric acid if disturbed (Fitzpatrick et al. 2006). Large-scale flood mitigation drains used for lowering the watertable in low-lying coastal areas during flooding have promoted sub-surface pyrite oxidation by the entrainment of atmospheric oxygen, resulting in acidic groundwater (Dent 1992; Indraratna et al. 1995). In addition, pyrite oxidation has been exacerbated by seasonal fluctuations of the watertable: when dry conditions dominate, the watertable drops and large volumes of soil are exposed to oxidising conditions. When rainfall recharges the groundwater following mainly dry periods, the release of acidic plumes from the soil in turn mobilises iron (Fe) and aluminium (Al) ions into the groundwater (Dent 1992), leading to even greater environmental problems such as significant damage to agriculture and aquaculture, degradation of steel and concrete infrastructure, and clogging of waterways (Indraratna et al. 2005).

Serious research for controlling pyrite oxidation in ASS had not been conducted until numerous fish were found dead because of low pH, low dissolved oxygen content and high amounts of soluble aluminium in coastal rivers in the 1980's although the impact of ASS was initially recognised in Australia in the early 1970's. Several techniques such as one-way

floodgates and modified two-way floodgates have been used successfully in coastal lowland in southeastern NSW, Australia, for preventing pyrite oxidation and treating the resultant acidic groundwater (Indraratna et al. 2005). Weirs installed in the drains succeeded in raising the phreatic surface in the surrounding area by maintaining higher and steady water levels in the drain (Blunden and Indraratna 2000), whereas two-way floodgates allowed tidal ingress of brackish creek water to enter into the drain during high tides in addition to maintaining steady water levels during low tides. Such entrance of brackish water with carbonate and bicarbonate ions improved the drain-water quality significantly due to buffering effects on the acidic drain-water (Glamore and Indraratna 2004). However, these techniques could not improve the long-term groundwater quality; rather, they increased the risk of flooding in low-lying areas with poor drainage (Indraratna et al. 2005).

In the south coast of NSW, local government agencies and councils are in search of alternative for spot treatment of strategic location in acid sulphate soil terrain to protect the agriculture, aquaculture (fish and oyster farming) industries, and to improve the water quality of the nearby drains. The application of active treatment systems such as pump-and-treat methods, direct addition of lime to streams and open lime drains have also been used in the past for the remediation of acidic water. However, they are not suitable for large areas due to high operation and maintenance costs (Komnitsas et al. 2007). Recently, attention has been paid to the use of permeable reactive barriers (PRBs) for remediating contaminated groundwater. PRBs represent a valid alternative to these traditional systems used in the south coast of NSW because of advantages such as no energy consumption, minimal operation and maintenance costs, and minimal disruption to the existing land use (Gavaskar 1999).

Although PRBs have been used worldwide for the remediation of contaminants such as chlorinated organic compounds, chromate, radionuclides and heavy metals (Blowes et al.

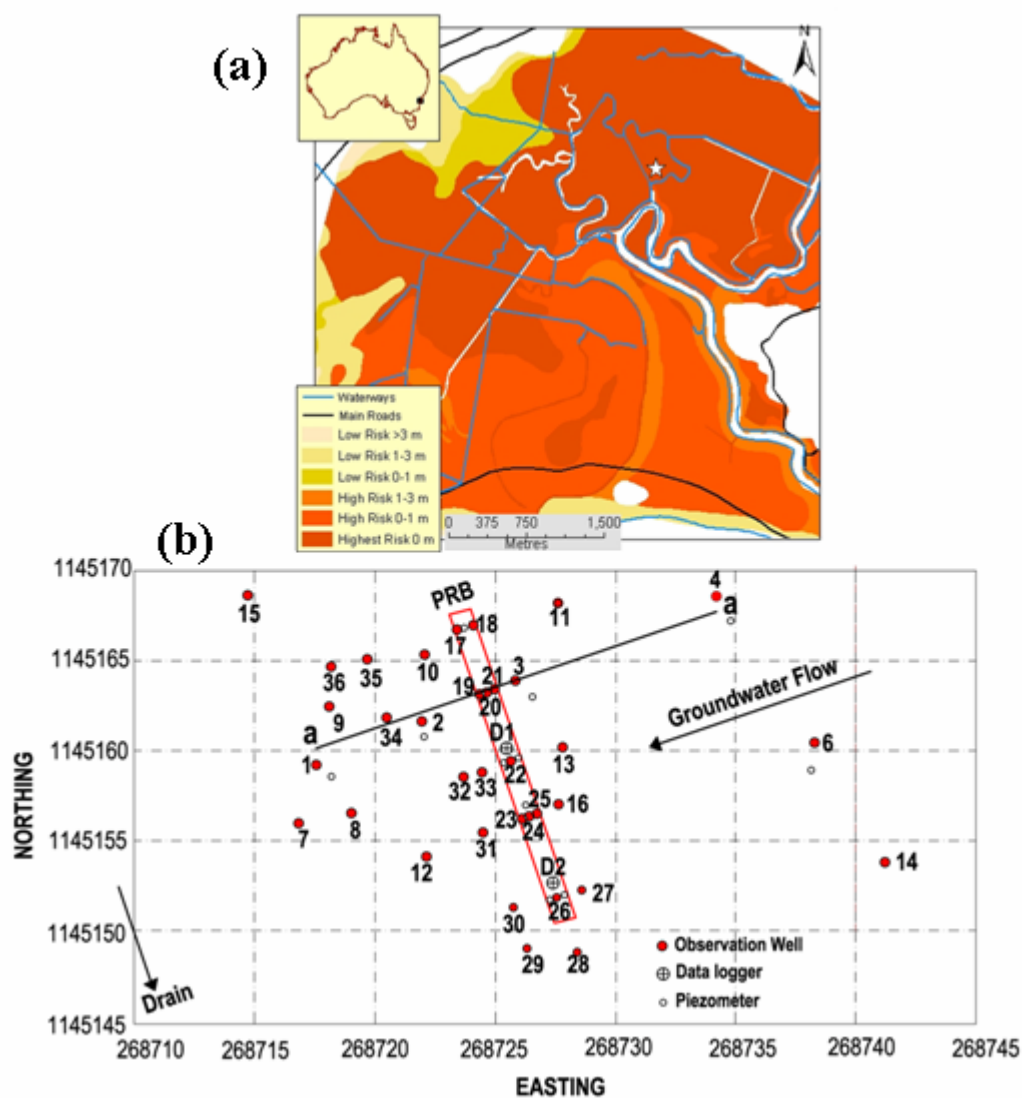
1997; Gu et al. 1999; McMahon et al. 1999; Powell et al. 1995; Puls et al. 1999a,b; Scherer et al. 2000; Vogan et al. 1999), their application for curbing ASS problems has been very limited to date, except for one trial open limestone drain reported by Waite et al. (2002) which failed in a short period of time possibly because of rapid armouring and clogging by precipitates due to the presence of oxidising conditions. Several researchers (Karvonen 2004; Komnitsas et al. 2007; Li and Benson 2005; Liang et al. 2003; McMahon et al. 1999; Puls et al. 1999a; Sarr 2001; Vogan et al. 1999; Yabusaki 2001) have reported that armouring on the surface of reactive materials and chemical clogging of pores, by precipitated compounds during chemical reactions inside the PRB, decrease the long-term performance parameters such as reactivity, porosity and permeability. Significant concerns relating to precipitation of iron and aluminium oxides and hydroxides also exist in alkaline PRBs with acidic groundwater in ASS terrain because their solubilities are pH-dependent. In addition, the precipitation of ferric oxyhydroxides can also result in generation of acidity (Waybrant et al. 1998) further reducing the efficiency and may affect the flow-path due to the clogging effects of accumulated precipitates (Sun et al. 2000).

Selection of the reactive media for a PRB is also of paramount importance, with particular reference to reactivity. Batch tests of 23 reactive materials were conducted in the laboratory, as reported by Golab et al. (2006). Following on from these studies, recycled concrete was selected for determining its reactive potential using a long-term column test because it is a waste and readily available material. The objective of the current research is to evaluate the performance of a PRB for neutralising acidic groundwater, which will address (i) study of the efficiency of the materials for improving the groundwater quality by a long-term column test under dynamic flow conditions, and (ii) the performance investigation of a pilot scale PRB, over the last two and a half years focussing on the geochemical factors such as armouring and chemical clogging that govern the long-term performance of the PRB.

## MATERIALS AND METHODS

### Site description

The investigated site is located in farming land situated in the Lower Shoalhaven floodplains area, near Bombaderry in southeastern NSW, Australia (Figure 1a). The site is adjacent to a flood mitigation drain that flows into Broughton creek, a tributary of Shoalhaven River adjacent to a drainage channel.



**Figure 1.** (a) Location of the study area, southeastern NSW, with PRB site marked with a star and ASS risk of soils is shown. (b) Layout of the PRB with transect “a-a” marked.



Baseline monitoring of the study site was carried out for over a year prior to installation of the PRB for the purposes of site characterisation. Some parameters that were studied include: monitoring of variations in the phreatic surface, monitoring of variations in the chemical composition of the groundwater, analysis of soil hydraulic conductivity, porosity and grain size, and the use of geophysical techniques to estimate the hydraulic conductivity of the area. A location about 15 m away from the drain was selected for the installation of the pilot scale PRB (Figure 1b) based on the results of site characterisation. The site has the following properties favourable for the installation of the PRB:

- 1) The groundwater is acidic with high Al and Fe levels (Table 1),
- 2) The site is low-lying (0-1 m Australian Height Datum (AHD)) and therefore not suitable for the use of weirs or two-way floodgates,
- 3) A drain is present nearby for the treated groundwater to flow into,
- 4) No man-made structures are present at the site, and
- 5) A zone of preferential groundwater flow exists at the site that the PRB can intercept.

### **Column Test**

The recycled concrete used in this study was collected from a refuse depot, i.e. a waste material discarded after demolition of around 25 year old concrete elements in the process of road expansion in rural NSW. The large recycled concrete fragments were crushed to make smaller fragments suitable for the column experiment. The particle size distribution (PSD) of the reactive materials used in the column was uniformly graded aggregates, predominantly in the range between 1.18 mm and 10 mm. The laboratory column test was carried out in a Perspex column (65 cm length, 5 cm internal diameter) fitted with several sampling ports to

monitor the efficiency of the reactive media for neutralising synthetic acidic groundwater in a controlled environment. The column influent was synthetic acidic water that simulated the average geochemical characteristics of the groundwater in ASS terrain measured fortnightly for six months from four observation wells (OW3, OW4, OW6, OW11) located up-gradient to the current location of PRB (Table 1 and Figure 1b).

**Table 1.** Average groundwater chemistry of four wells (OW3, OW4, OW6, OW11) over six months prior to installation of the PRB.

Parameters		Groundwater
pH		3.7±0.6
Na <sup>+</sup>	(mg/L)	467.3±176.2
K <sup>+</sup>	(mg/L)	48.4±11.6
Ca <sup>2+</sup>	(mg/L)	141.9±52.7
Mg <sup>2+</sup>	(mg/L)	147.0±65.4
Al <sup>3+</sup>	(mg/L)	18.0±14.6
Total Fe	(mg/L)	137.5±143.8
Cl <sup>-</sup>	(mg/L)	815±270.1
SO <sub>4</sub> <sup>2-</sup>	(mg/L)	1312.7±587.4

The crushed recycled concrete was packed in the column above a 5 cm sand layer with another 5 cm sand ball filter layer at the base; and with a 5 cm sand ball filter at the top of the column. The average total porosity of the reactive media in column was 0.52 (total pore volume was 534 mL). Steady upward flow of the influent was maintained through the column using a peristaltic pump with an average flow rate of 2.4 mL/min. Based on the flow rate, the retention time for one pore volume was 3.70 hours which is ~26 times smaller than the retention time for the estimated maximum groundwater flow rate of 30 cm/day in the field. Although the analysis of the precipitates would be useful to observe the neutralising capacity of the materials at different intervals, it is practically not possible to remove solid samples from the column during the experimental run. Therefore, only the water samples were collected from the sampling ports installed along the column walls, at a distance of 2.5 cm, 30 cm and 50 cm from the interface between the bottom sand layer and the recycled concrete

and also from the column outlet and analysed for pH, bicarbonate alkalinity Ca, Al and Fe concentrations. The samples were collected in duplicate. All chemical analyses were performed according to the standard method for water and wastewater examination (APHA 1998). In addition, Acid Neutralization Capacity (ANC) of the recycled concrete was calculated following the Acid Sulphate Soils Laboratory Method Guidelines 2004 (Ahern et al. 2004).

On completion of the experiment, the recycled concrete which was coated with precipitates was removed from the column and cut to produce a sharp edge in order to distinguish the coated surface from the inner uncoated concrete. The cut piece of the aggregate was examined by scanning electron microscope (SEM) and analysed by energy-dispersive X-ray spectroscopy (EDS) to characterise the precipitates coating the surface of the concrete.

### **PRB installation and performance monitoring**

Following the site characterisation and performance of reactive media in the column tests, a trial PRB was designed to maximise groundwater residence time within the PRB and minimise bypassing of the barrier. The optimum location was chosen running roughly parallel to a flood mitigation drain, around 15 m away from the drain, intersecting the zone of the maximum groundwater flow (Figure 1). On October 5, 2006, a PRB (17.7 m long, 1.2 m wide and 3 m deep) was installed in the Lower Shoalhaven floodplains area, near Bombaderry in southeastern NSW, Australia. The PRB was filled with crushed recycled concrete (40mm diameter) and the trench was lined with geotextile fabric to protect the reactive media from physical clogging by soil and other fine particles entering the barrier. A total of 30 observation wells and 12 piezometers were installed inside, up-gradient and down-gradient of the PRB (Figure 1b) to monitor phreatic surface variations, hydraulic gradients, permeability and groundwater chemistry. Groundwater elevation and water quality

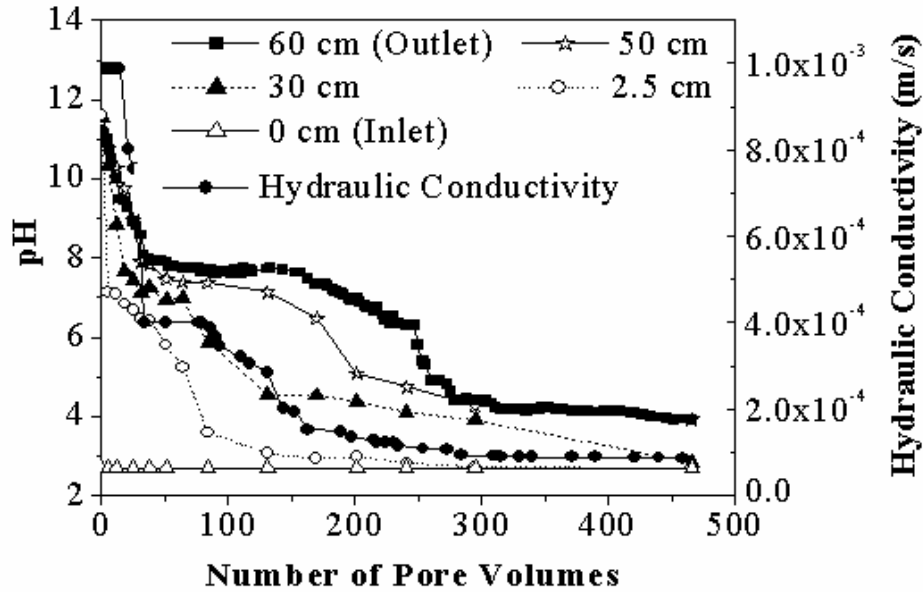
parameters such as pH, ORP, and temperature were directly measured in the field every month from October 2006 using water level meter and multi-parameter field electrode probes. Rainfall data are measured daily by a meteorology station within 5 km of the site. In addition, pH, dissolved oxygen (DO), water pressure and temperature were measured hourly by two multi-parameter automated data loggers installed within the barrier. Groundwater samples were collected frequently for analysis of iron, aluminium, major cations, anions and other trace metals. All chemical analyses were performed following the standard method for water and wastewater examination (APHA 1998).

## **RESULTS AND DISCUSSION**

### **Column Test Analysis**

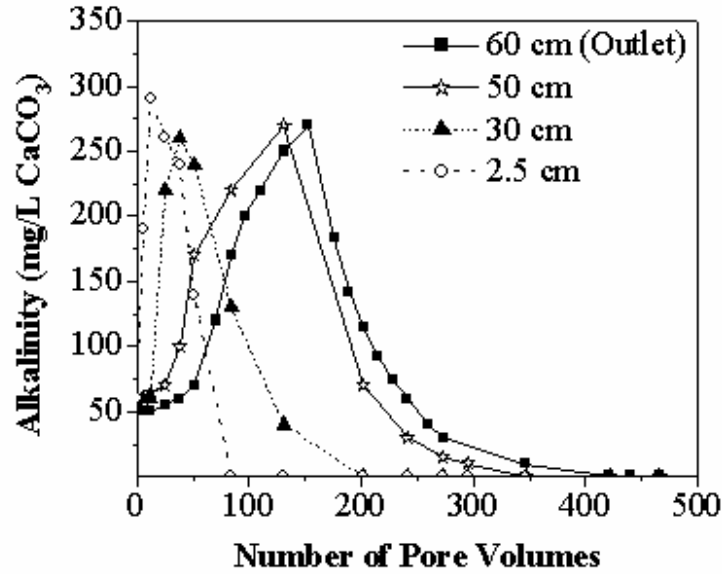
#### ***Water quality parameters***

The effectiveness of the reactive material was assessed with respect to the pH, bicarbonate alkalinity, Ca, Al and Fe concentrations of the treated water. Figure 2 shows that the effluent pH decreased rapidly from pH 12.1 to 7.9 within 38 pore volumes (PV), after which two long plateaus were observed: first a near-neutral plateau (pH ranging from 7.9 to 7.5) that continued until 156 PV, after which pH decreased slowly to a value of 7.0 at 200 PV and to 6.5 at 250 PV. After reaching a level of 6.5, the pH dropped abruptly reaching the second plateau at a pH~4, and then remained unchanged for many further pore volumes (466 PV).



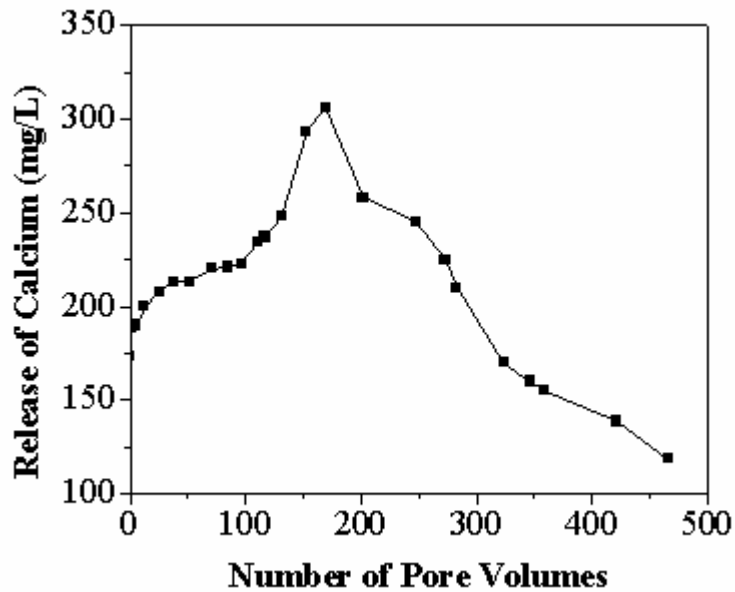
**Figure 2.** pH vs number of pore volumes passed for different sampling ports along the length of the column and changes in hydraulic conductivity of the recycled concrete.

The initial drop in pH (after 38 PV passed through the column) was assumed to be due to the depletion of carbonate alkalinity. Figure 3 shows that the bicarbonate alkalinity of the effluent was as low as 50 mg/L  $\text{CaCO}_3$  when the pH dropped to a steady state value. After that, the level of alkalinity started to rise slowly until it reached a peak value of 270 mg/L (as  $\text{CaCO}_3$ ) at ~180 PV. The gradual decreasing trend in pH was consistent with the depletion of bicarbonate alkalinity after 180 PV indicating that a decrease in efficiency of the reactive material probably started at that point. However, after reaching pH 6.5 at 250 PV, the pH fell to 4 until equilibrium with the most soluble hydroxide mineral was attained due to the depletion of carbonate minerals. Similar depletion mechanisms of carbonate minerals through the consumption by acid neutralisation reactions have also been documented by other researchers in acid mine drainage (Blowes and Jambor 1990; Cravotta and Watzlaf 2002; Johnson et al. 2000; Morin et al. 1988). In addition, Jurjovec et al. (2004) also reported a similar plateau of pH due to equilibrium of the effluent water with respect to gibbsite ( $\text{Al}(\text{OH})_3$ ) at pH 4.0 in the remediation of acid mine drainage.



**Figure 3.** Alkalinity generation vs number of pore volumes passed for different sampling ports along the length of the column.

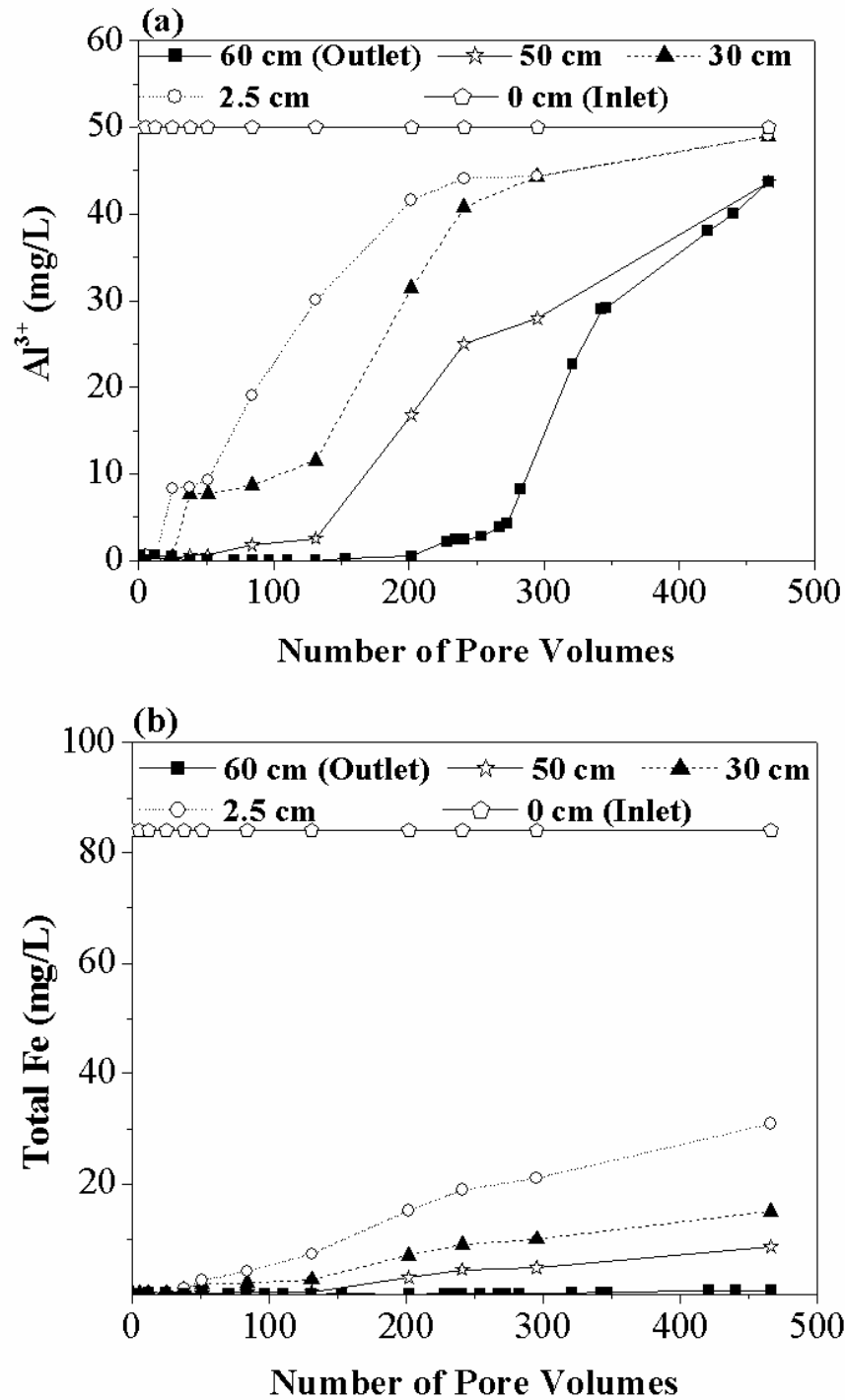
Because of the heterogeneous nature of this waste concrete, accurate characterisation of this material was not available. However, past local government council reports suggest that this ordinary Portland based concrete aggregates were of grades M25 and M30 with a water/cement ratio of 0.4-0.43. In addition, the chemical analysis showed that the crushed powder of the recycled concrete contained 68.8 g/kg Ca. The most abundant alkalinity generating minerals in the recycled concrete are cementitious minerals because of the presence of large amounts of calcium oxide in cement in different complex structures such as calcium silicate hydrated compounds (C-S-H) and calcium aluminosilicate hydrated compounds (C-A-H) as reported by Rahman et al. (1999). Dissolution of these minerals in the presence of CO<sub>2</sub> and moisture has the potential to generate substantial carbonate/bicarbonate alkalinity throughout their lifetime to bring the pH of the pore water to near neutral, releasing large amounts of Ca. Consequently, the release of Ca in the effluent was high (180 mg/L Ca<sup>2+</sup>) in the starting period of the experiment, increased to a peak of 300 mg/L at ~170 PV and decreased (Figure 4), coinciding with the plot of alkalinity generation.



**Figure 4.** Released calcium in outlet of the column vs number of pore volumes passed.

### *Removal of aluminium and iron*

Most of the Al contained in the synthetic groundwater precipitated rapidly during the initial phase of the experiment due to the high pH, because, Al begins to precipitate when the pH rises above 4.5 (Figure 5a). Al was observed in the effluent water for the first time when the pH of the effluent dropped from 6.9 to 4 (after ~250 PV), and the concentration continued to increase because of its high solubility at pH<4. The abrupt increase in the concentration of Al<sup>3+</sup> was observed to coincide with the depletion of bicarbonate alkalinity and abrupt decrease in pH after 250 PV. Similarly, Fe also precipitated when the pH exceeded 3.5. Until 466 PV, the effluent pH did not drop below pH 3.5; accordingly, the Fe content of the effluent (0.62 mg/L) was negligible throughout the duration of the column test (Figure 5b). Although both Fe and Al removal rates decreased with time, Fe concentration observed in effluent was very low compared to that of Al until the end of the experiment (466 PV). This confirmed that the PRB using recycled concrete would remove Fe more effectively than Al.

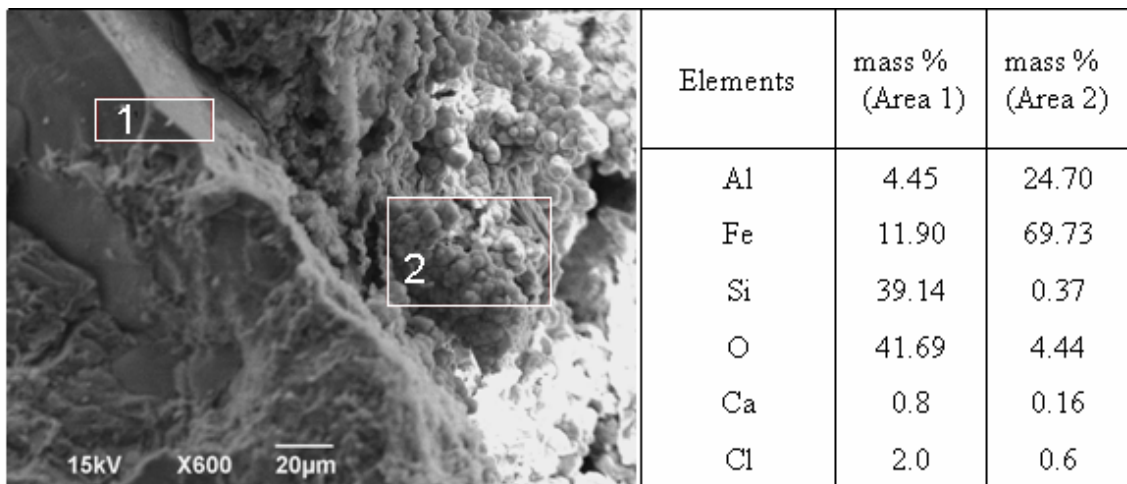


**Figure 5.** (a) Al and (b) Total Fe concentrations vs number of pore volume passed for different sampling ports along the length of the column.

At a near neutral pH condition maintained by the carbonate/bicarbonate buffering in the column test, the precipitation of amorphous aluminium and iron hydroxides and



oxyhydroxides is favoured, indicated by the decrease in Al and Fe concentrations in the effluent. Comparison of the large amount of precipitates of iron and aluminium minerals on the surface of aggregate with a clean surface (surface with no precipitates at the sharp cut edge) of the same aggregate observed in SEM analysis and their amounts in EDS (Figure 6) confirms the coating of the surface by iron and aluminium precipitates in the form of hydroxide and oxyhydroxide forms (H is not detected by EDS).



**Figure 6.** SEM/EDS analysis of a small cut piece of armoured recycled concrete removed from the column after completion of the experiment.

### *Longevity Prediction*

Armouring on the surface of the recycled concrete can result in a decrease in the rate of mineral dissolution, finally decreasing the acid neutralisation capacity of the materials. The experimental observations imply that the lower part of the column that became coated with precipitates, lost part of its reactive efficiency due to:

- 1) decreasing trend of pH from the base of the column upwards (Figure 2);
- 2) rapid alkalinity generation and depletion after few pore volumes (Figure 3); and
- 3) increasing concentration of aluminium and iron (Figure 5) with distance travelled inside the column with increasing pore volumes.

However, continuous alkalinity generation in the upper part of the column still added alkalinity to the system over a long period (250 PV) indicating that the efficiency decreases slowly with the distance travelled. In the column test, the 250<sup>th</sup> Pore Volume was selected as the baseline for predicting the longevity of the materials based on pH of 6.5, the increase in Al<sup>3+</sup> concentration in solution and the decreasing trend of Ca<sup>2+</sup> released. Total ANC of the crushed samples of reactive media is 145 mg/g CaCO<sub>3</sub> equivalent. Corresponding to this ANC, the total concrete of 1.22 kg used in column had a capacity to neutralise 518 PV of the acidity of synthetic water (645 mg/L CaCO<sub>3</sub>) used in the column test. However, the rapid drop in pH and alkalinity after ~ 250 PV indicates that the material's efficiency was lost by nearly 50% by the armouring of reactive media and nearly the same amount by the exhaustion of the alkalinity of the material corresponding to that pore volume. In contrast, the hydraulic conductivity of the reactive material during the test decreased by only tenfold (Figure 2) reaching 10<sup>-4</sup>m/s, and was still maintained at a higher level than that in natural soil in the field (10<sup>-5</sup>m/s). Therefore these column test results indicate without any doubt that armouring is more significant than clogging of pores for reducing the longevity of the PRB.

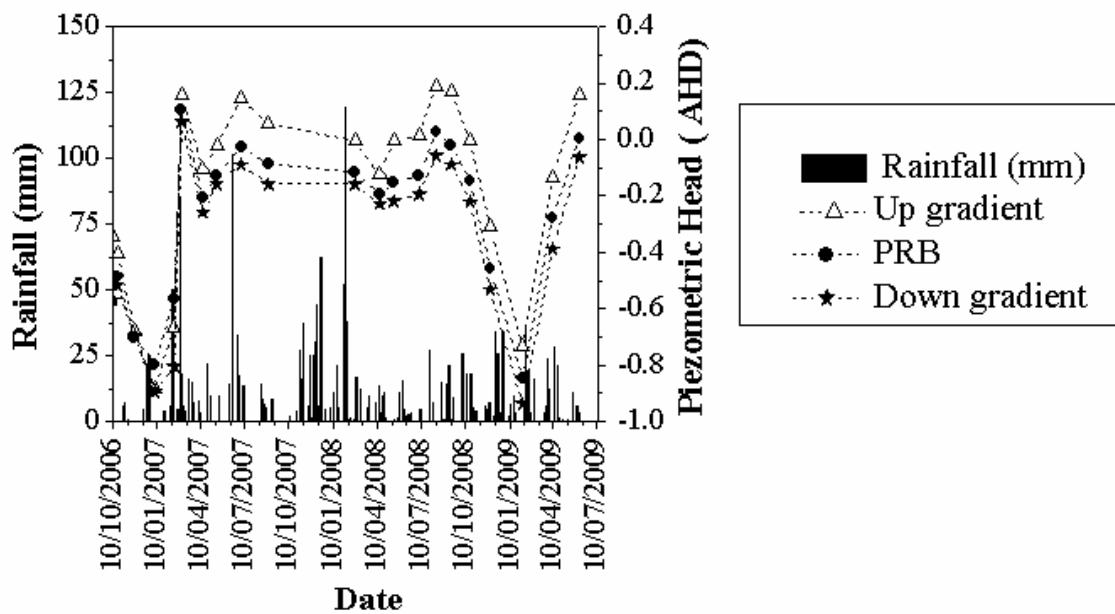
The synthetic water used in this column test (pH~2.68 and acidity 645 mg/L CaCO<sub>3</sub>) was slightly more acidic than the groundwater in the field (average pH ~3.7 and average acidity ~550 mg/L CaCO<sub>3</sub>). The impact on longevity of the materials of other parameters such as particle size distribution and porosity of the materials could not be considered here. Considering the effects of retention period, armouring and the acidity of the synthetic water used in this study, the longevity of the PRB would vary from 3 to 8 years depending on the variation of flow rate from 30 cm/day to 10 cm/day. However, the lower acidity in the field compared with the column test indicates that recycled concrete in the field would treat the acidic water for a longer period, fulfilling the expectations of the local government for improving water quality to protect the aquatic environments of nearby surface water sources.

In addition, the longevity of the PRB further depends on the amount of concrete used and the seasonal changes in field. The mass of the concrete used inside the PRB is 80 tonnes, corresponding to which the theoretical total acid neutralization capacity of the PRB is 11.6 tonnes. Depending on the flow rate variation (10 cm/day to 30 cm/day), the amount of acid passed through the PRB per year is estimated to be  $\sim 1100 \times 10^3$  L to  $3200 \times 10^3$  L and the alkalinity consumption is predicted to be  $\sim 0.6$  tonnes to 1.75 tonnes per year respectively. But, it has been noted from the column experiment that armouring will be a more significant issue for the PRB than exhaustion of the acid neutralizing capacity of the reactive material. To ensure that excess armouring of aggregates would not prematurely shorten the PRB's effective lifespan, the longevity of the PRB in the field has been continuously monitored.

### **Hydraulic Evaluation of the Study Area**

The study area is characterised by a shallow groundwater zone in an unconfined aquifer with groundwater levels ranging from approximately 0.5 to 1.8 m below ground surface, and fluctuating by an average of 0.3m seasonally in response to winter precipitation or dry periods. The hydraulic conductivity of the study area was  $10^{-5}$  m/s, whereas the hydraulic conductivity of the recycled concrete used in PRB was in the range of 10 to  $10^{-1}$  m/s. The groundwater flow rate was estimated to vary from 0-30 cm/day depending on the seasonal variation of the weather. Prior to the installation of the PRB in the field, the piezometric head was steady in a range of  $-0.3$  m to 0 m AHD. Notable declines in the watertable were observed in the study area immediately after installation of the PRB until the next heavy rainfall in February 2007 (Figure 7). This is thought to be a result of (a) change in hydraulic gradient by dewatering due to the construction of the trench for the PRB, (b) water suction capacity of unsaturated recycled concrete used inside the PRB, forcing the PRB to act as a sink until it became fully saturated, and (c) a lack of rainfall. The instability in the flow

pattern, especially in down-flow of the PRB resulted in variable water quality down-gradient of the PRB until the material became saturated (Figure 7) by heavy rainfall in March 2007. Since then, steady groundwater flow has been observed from up-gradient to down-gradient of the PRB, as indicated by the parallel hydraulic head in different piezometers over time. The fluctuation in watertable after reaching steady-state flow has been governed by the variation of the weather (rainfall and evaporation) and the infiltration capacity of the soil.



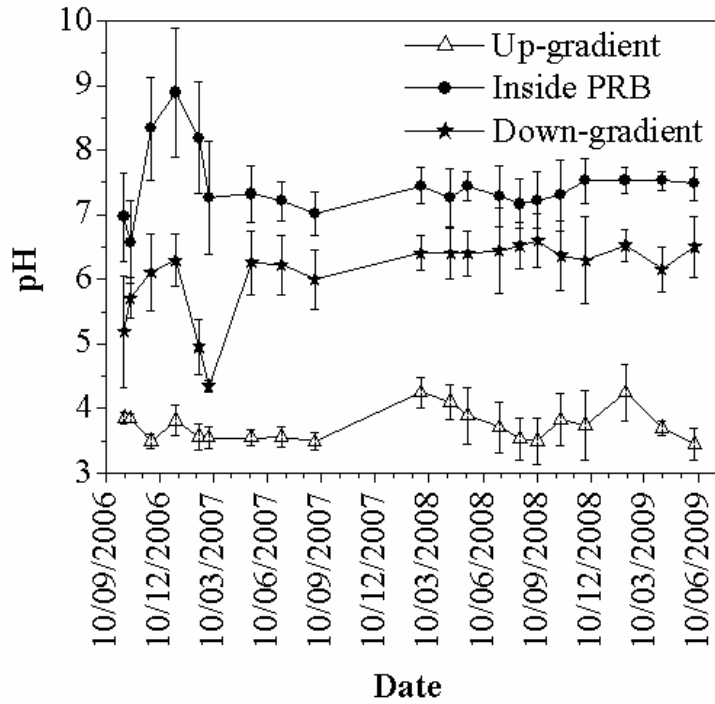
**Figure 7.** Piezometric head variation at the PRB site with respect to rainfall events.

### **Performance Parameters of the PRB**

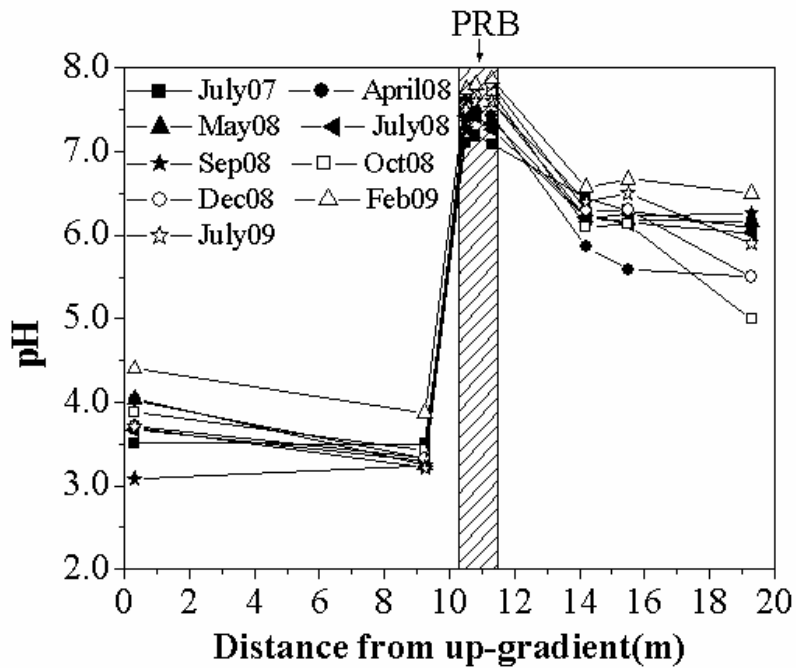
Up-gradient of the PRB, the groundwater is acidic (pH 3.2 to 4.5; average 3.7 over the study period) and varied depending on: (i) dilution by large rainfall events and (ii) flushing of acid by small rainfall events following dry periods. During dry periods, the watertable drops and the pyritic layer is exposed to oxidation; hence during small rainfall events following a dry period, sulphuric acid is contained in the soil. The soil up-gradient of the PRB is generally aerobic, as represented by high positive ORP values up to 530mV and the low ratio of

chloride to sulphate (0.3) observed in the up-gradient groundwater illustrates that pyrite oxidation is occurring. Under such acidic conditions, the groundwater contains high amounts of Al and Fe (Tables 1 and 2).

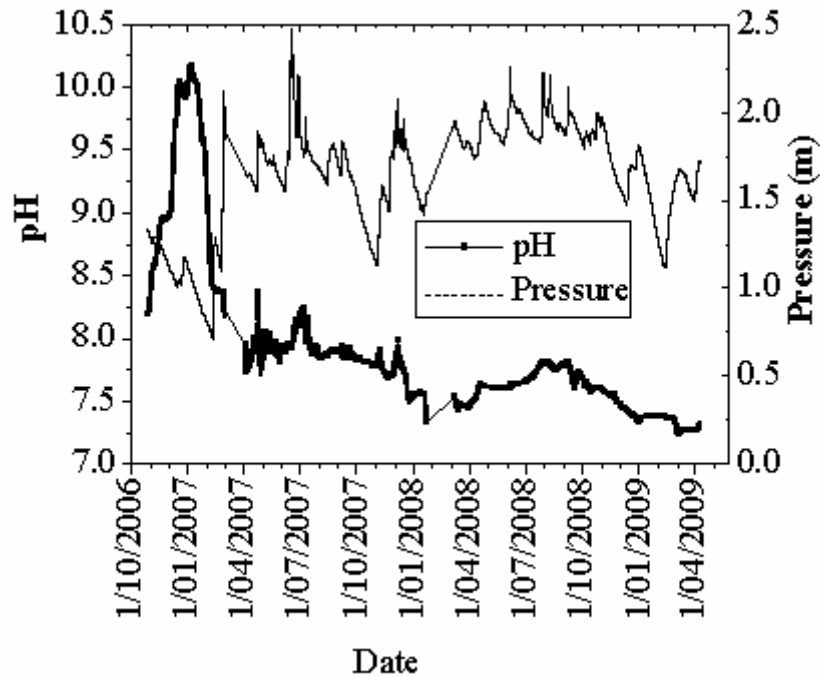
The groundwater inside the PRB has consistently been alkaline to neutral (pH 10.2 to 7.3) with low ORP values (down to  $-297$  mV) for the past two and half years of operation once it became fully saturated indicating that reducing conditions were dominant for the dissolution of alkaline minerals from the reactive media. The difference in pH between groundwater up-gradient of the PRB, and that inside the PRB and down-gradient of the PRB of the last two and half years illustrates that the PRB performed well in the field for neutralising acidic water (Figures 8 and 9). Average pH was above 7.3 and 6.0 inside the PRB and down-gradient respectively at the end of two and half years. The maximum pH value achieved by the reactive media in the field is consistent with the column test results confirming the release of carbonate alkalinity for  $\text{pH} > 8.3$  during the early stages after installation of the PRB because of the high acid neutralising capacity of the concrete. The plateau of pH in the neutral range (pH 7.3; two and half years after installation) and high rate of alkalinity generation (210-400 mg/L  $\text{CaCO}_3$ ) at different observation points inside the PRB confirms that recycled concrete has been working as a good neutralising material for acidic water in a similar manner to the controlled environment in the column test despite the variable environmental conditions experienced in the field. However, the pH of the PRB has been decreasing slowly, comparable with that in the column test, due to exhaustion of the alkalinity generating materials as well as assumed fouling by precipitates over the surface of the materials (Figure 10).



**Figure 8.** Temporal variation of the average groundwater pH up-gradient, inside and down-gradient of the PRB. The averages represent readings from 30 observation wells: 8 up-gradient, 10 inside the PRB and 12 down-gradient.



**Figure 9.** pH of the groundwater after installation of the PRB along a transect a-a at different time intervals.



**Figure 10.** pH and groundwater pressure inside the PRB measured by a data-logger.

Down-gradient of the PRB, the pH could not improve immediately after installation of the PRB due to variability in groundwater flow patterns. However, upon reaching steady-state flow in February 2007, the average pH started to increase and reached up to 6.2. The lower pH in the down-gradient as compared with that inside the PRB is due to: (i) dilution of the effluent from the PRB and (ii) occasional mixing of acid generated in the soil because the PRB cannot control acid generation in the soil by pyrite oxidation. The ORP readings down-gradient of the PRB (14 mV to 458 mV) indicate mostly aerobic conditions favouring pyrite oxidation. Nevertheless, despite the spatial and temporal variation of groundwater pH down-gradient of the PRB, it has been improved significantly by the recycled concrete used in the PRB.

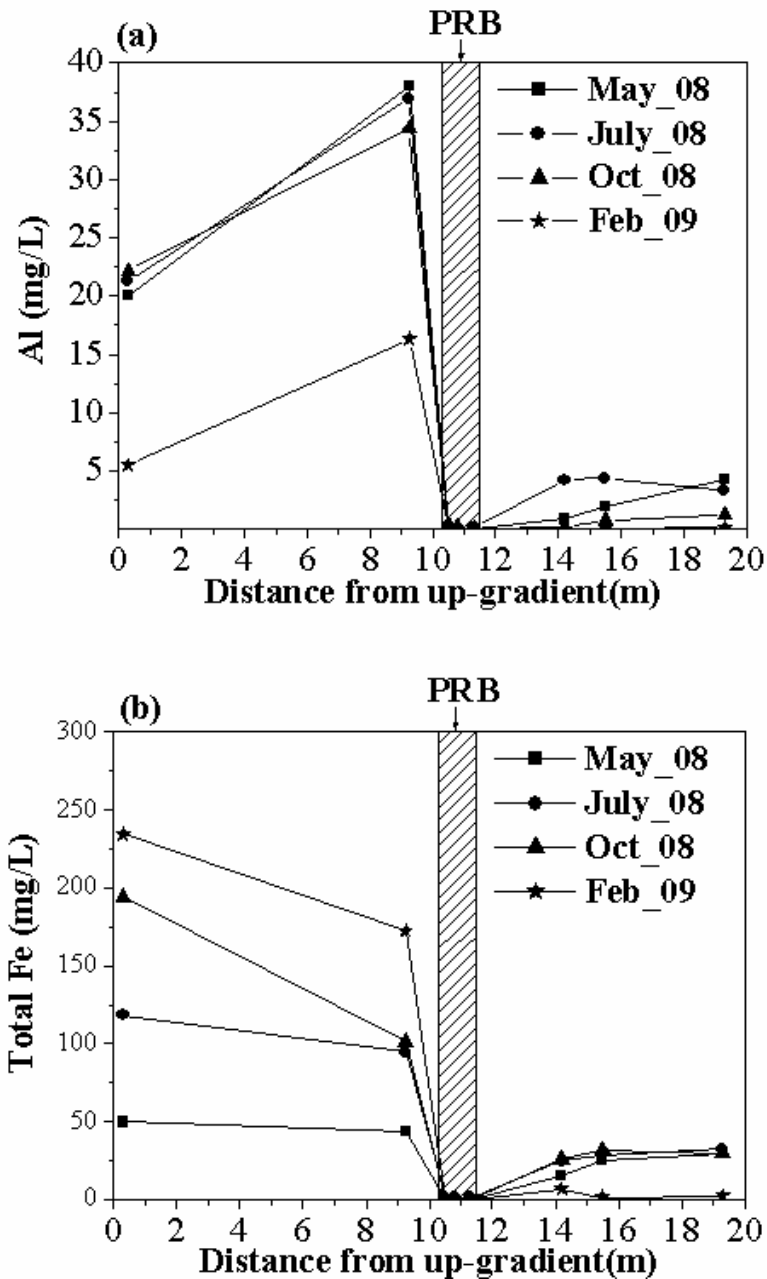
## Removal of Iron and Aluminium

The untreated groundwater of the study area is acidic and has high concentrations of dissolved Al (~ 40 mg/L) and Fe (~ 250 mg/L) (Figure 11). Most of the Fe and Al contained in the groundwater precipitated rapidly when alkaline minerals from the recycled concrete started to dissolve and increased the groundwater pH. Frequent monitoring of Fe and Al present in the groundwater of the PRB shows that most of Fe and Al precipitated rapidly, probably in their hydroxide and oxyhydroxide forms, further generating alkalinity into the system, thereby increasing the pH to near neutral values (Table 2 and Figure 11). The maintenance of the total Fe and Al concentration below average values of 2 mg/L and 0.5 mg/L, respectively, inside the PRB over the two and a half year period indicates the excellent removal efficiency of recycled concrete for Fe and Al.

**Table 2.** Average chemistry of the groundwater associated with the PRB for two representative time intervals. The data are averaged from 8 wells up-gradient and 10 wells inside the PRB.

Ions	Jul-2008		Oct-08	
	Up-gradient (mg/L)	Inside PRB (mg/L)	Up-gradient (mg/L)	Inside PRB (mg/L)
Na <sup>+</sup>	361.48	413.23	385.30	389.01
Ca <sup>2+</sup>	114.36	276.53	115.15	315.70
Mg <sup>2+</sup>	86.86	84.29	102.19	79.00
K <sup>+</sup>	33.82	32.72	37.15	33.16
Total Fe	90.54	0.73	142.64	1.99
Al <sup>3+</sup>	28.42	0.09	29.28	0.97
Cl <sup>2-</sup>	558.35	527.36	497.89	486.32
SO <sub>4</sub> <sup>2-</sup>	1008.46	944.69	1129.44	1017.11
HCO <sub>3</sub> <sup>-</sup>	0.00	146.17	0.00	232.00





**Figure 11.** (a) Al and (b) Total Fe concentrations of the groundwater after installation of the PRB along a transect a-a at different time intervals.

The concentrations of Fe and Al increased with distance down-gradient of the PRB. This is likely due to the active and ongoing oxidation of pyrite in the soil, generating fresh acid, which releases Fe and Al into the groundwater. During rain events the treated groundwater from the PRB would mix with the *in situ* acidic groundwater, thus causing an increase in Fe and Al levels and decrease in pH. It is also likely that some untreated groundwater from the

top, bottom and sides of the PRB flows into the down-gradient monitoring area. Therefore, although the PRB cannot prevent the further oxidation of pyrite in the soil, the treated groundwater leaving the PRB can improve the down-gradient water quality. The effectiveness of PRBs in ASS terrain could be improved if constructed in series and a funnel-and-gate design is used to decrease the risk of mixing with untreated groundwater.

### **Longevity of PRB**

Column test results suggest that all the Fe and Al ions in groundwater precipitate out due to high ANC of recycled concrete during the early stage until the pH drops rapidly from a neutral value. During the first 18 months from the time of PRB construction, the Fe and Al concentrations of water specimens inside the PRB were measured to be zero in presence of alkaline to near neutral pH, matching with column test. Since then, now at 30 months, average Fe and Al levels within the PRB are still nearly zero (< 5 mg/L). However, slight fluctuation in the pH has been observed inside the PRB. Comparison of the water chemistry indicates that the PRB has removed Fe and Al effectively (more than 95%), with a constant rate of release of Ca and almost no change in other remaining ions (Table 2). Similar to our studies, Robbins et al. (1999) also reported that sulphate levels were unchanged in limestone drainage for concentrations less than 2000 mg/L, resulting no sign of gypsum precipitation as the activities of Ca and  $\text{SO}_4^{2-}$  were not high enough to reach the solubility product of gypsum. The concentrations of trace elements were already low up-gradient of the PRB (Table 3) although some exceed the ANZECC (2000) guidelines for fresh and marine water quality. In all cases, the PRB caused a decrease in the concentration of the trace elements measured but this decrease did not bring the levels below the ANZECC limits in all cases.

The Al and Fe probably precipitated out of solution as hydroxides or oxyhydroxides inside the PRB, as was indicated by the SEM results from the precipitates formed in the column test.

The overall groundwater chemistry of the PRB, along with the column test, shows that Fe and Al are the dominant ions likely to cause the deterioration in performance of the PRB. Even after two and half years, the PRB maintains a high level of efficiency for removing Fe and Al from the groundwater indicating that large amounts of precipitates must have formed. The precipitates are probably causing armouring on the surface of the reactive materials, as observed in the column test. The brown-yellow coating observed on the surface of the data loggers 18 months after installation, indicated that armouring is occurring due to those precipitates. The slight increase in the concentrations of Fe and Al in the latter stage of the two and half years period compared to the installation period also demonstrates that armouring effects have been just initiated. However, the steady piezometric head within the PRB over the two and half years monitoring period after attaining steady state conditions in February 2007 (Figure 7) shows that the hydraulic conductivity has not been decreased significantly. The continuous mineral precipitation inside the PRB over time indicates that the effectiveness of the PRB may decrease rapidly in the near future due to the decreased surface area of the concrete by armouring effect, further decreasing the longevity of the PRB.

**Table 3.** Groundwater trace metals content measured in October 2008 compared with the upper limits of the ANZECC (2000) guidelines for fresh and marine water quality. The data are averaged from 8 wells up-gradient and 10 wells inside the PRB. **N/A: not applicable.**

Ions	Up-gradient (mg/L)	Inside PRB (mg/L)	ANZECC upper limit (mg/L)
Ag	<0.001	<0.001	N/A
As	0.007	0.005	0.024
Cd	0.002	<0.001	0.0002
Cr	0.005	0.004	0.001
Cu	0.010	0.003	0.0014
Mn	1.277	0.428	1.9
Ni	0.140	0.018	0.011
Pb	0.006	0.002	0.0034
Zn	0.424	0.018	0.008
Hg	<0.001	<0.001	N/A

## CONCLUSIONS

This paper presents the findings of the first PRB using recycled concrete for the spot treatment of acidic groundwater in acid sulphate soil terrains. The trial PRB is located in the Shoalhaven region in southeastern NSW, Australia. Alkaline materials are suitable options for use in PRBs for treating acidic groundwater and for the current PRB recycled concrete was selected as the most suitable, cost-effective reactive material through a long-term column test.

Column test results confirm that treatment of highly acidic groundwater creates adverse conditions within the reactive media accelerating the reduction of reactivity and the effective lifetime of a PRB system due to the fast consumption of alkalinity and decrease of the surface area of the reactive materials by the precipitation of various compounds of aluminium and iron. The longevity of the reactive media can decrease up to 50% due to armouring effects. However, it appears that chemical clogging is not significant as relatively constant hydraulic conductivity can be maintained throughout the duration of the long-term column tests.

The performance of the PRB was evaluated on the basis of pH measurement over a two and half year period. The recycled concrete used as the reactive media within the PRB has effectively maintained neutral pH and removed the main groundwater contaminants namely iron and aluminium. Monitoring of the groundwater quality inside the PRB confirms that the water chemistry is primarily controlled by the alkalinity generation by dissolution of lime and other alkaline minerals in the concrete and the precipitation of insoluble Al- and Fe-hydroxides and oxy-hydroxides, supporting the column test results. The capacity of the barrier to continue to remove Fe and Al depends on the following factors:

- (a) variation of the acidity of the groundwater due to pyrite oxidation;

- (b) long-term generation of alkalinity by the minerals present in the recycled concrete;  
and
- (c) reduction of the reactive surface area by armouring effects due to precipitated  
minerals

Overall, the PRB has performed well but slight decreases in the pH and Fe and Al removal efficiencies indicate that some armouring of the surface of the reactive media has occurred and affected the reactivity of the recycled concrete. In contrast, chemical and physical clogging has negligible effects on the groundwater flow characteristics of the PRB as reflected by a steady piezometric head within the PRB throughout the monitoring period.

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